INCREASING THE ACTIVITY OF COAL MINERAL MATTER
FOR HYDRODESULFURIZATION AND HYDRODENITROGENATION

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Catalysis by coal minerals has been the subject of much work in recent years by Guin et al. (1,2), Granoff, et al. (3,4,5), Given and coworkers (6,7), and Mukhejce and Chowdhury (8) since its discovery by Wright and Severson (9) in 1972. Several studies using model compounds such as thiophene, benzothiophene, pyrrole, pyrrolidene, and n-butyl amine have also been published based on work performed at the University of Kentucky (10-16). It is the purpose of this paper to compare the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activities of mineral matter modified by iron or nickel additions to the activities of untreated mineral matter.

EXPERIMENTAL – A pulse micro-reactor packed with mineral matter using hydrogen as the carrier gas was used to evaluate catalytic activity over the temperature range of 573 to 723 K at 101 kPa. Conversions were calculated from the total of C_4 gases detected in the product stream by gas chromatography. Details of the system are presented elsewhere (16). Modification of mineral matter was carried out by preparing physical mixtures of Ky #9 and Ky #11 with Harshaw Ni-4301 (6% Ni and 19% W as oxides on silica-alumina) and by evaporating various iron and nickel solutions containing Ky #9 and Ky #11. Physical mixtures were prepared in two different ways. In one method H_2-pretreated, −24+42 mesh particles of LTA and the Harshaw catalyst were combined to give 10 w/o nickel and loaded into the reactor for activity testing. The activity was between that of the LTA and the catalyst. A second physical method was used which gave more interesting results. The catalyst was ground in a mortar and pestle and combined with either of the LTAs, pressed, crushed to −24+42 mesh, and H_2 pretreated as for other test samples. The catalyst charged was 5 x 10^{-4} kg containing 10 w/o nickel (calculated).

Two grams of LTA were mixed with the corresponding amount of $Ni(NO_3)_2 \cdot 6H_2O$ to give 10, 25, and 50 w/o Ni mixtures. A small quantity of double distilled water (0.021) was added to dissolve the salt. If necessary, heat was added for about 30 seconds to carry out the dissolution. The slurry was then placed in a 383 K oven overnight to evaporate the liquid. The remaining solid was pressed, sieved, and pretreated as described earlier. Similar treatments were carried out with $FeCl_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and $NiCl_2 \cdot 6H_2O$.

RESULTS AND DISCUSSION - The HDN conversion for the combination of the Ky #11 LTA with the ground Harshaw catalyst is shown in Figure 1, along with the pure components. On the left is the Ky #11 LTA showing total conversion along with the amount of butane and unsaturates. This contrasts sharply with the catalyst which produces only butane, gives lower conversion, and loses activity as pulsing continues. The mixture (3rd graph from left) pro-

duces a mean conversion of 72.5 which is much higher than either of the components indicating a synergistic effect. The first pulse produced only butane but thereafter the butane accounted for about 12.5%, 1-butene for about 9%, and 2-butenes for about 51% of the total 72.5% conversion. Apparently, the hydrogenation sites are quite sensitive to nitrogen poisoning, but they do not affect the denitrogenation activity.

The effect is even more impressive when Ky #9 which was third lowest in activity was combined with the powdered catalyst. As shown in Figure 2, the mixture (right graph) gave a mean conversion of 77.2% which was the highest of any material tested. Again the first pulse gave pure butane; thereafter about 32% (of the 77.2%). After five pulses cis-2 butene appears and is about the same value as butane with the remainder trans-2-butene. No 1-butene was observed.

The catalyst produced from $Ni(NO_3)_2$ $6H_2O$ and Ky #11 evidenced quite stable performance with a mean conversion of 53.6% which is very close to the LTA value (Figure 1). Unsaturates make up almost all of the products.

Results for all of the Fe and Ni solution-type catalyst are presented in Table I which gives both HDN and HDS conversion. None of the mixtures improve the HDN conversion appreciably and the ferric nitrate decreases it by 26%. Very large changes in HDS conversion are apparent since the LTA gives <1% and the 50% Ni yields a value of 38.8%. The values of the surface area for the Ni treated mixtures give a mean value of 28.9 m^2/g $\pm$ 2.2 which is slightly less than the untreated LTA value of 32.0. This indicates the added Ni is responsible for the increase in activity and the surface area is unaffected by the treatment. The iron treatment shows some improvement as does the nickel chloride, but the nitrate is by far the most effective treatment rivaling the Harshaw mixtures as shown in Figure 3. Here it is seen that 10% Harshaw with Ky #11 gives 23% conversion compared to 21% for the above treatment. The highest HDS conversion was 24.2% for the Ky#9-Harshaw mixture. It is also interesting to note that the Harshaw catalyst does not give a high concentration of n-butane as it did for HDN. Probably H_2S poisoning is responsible for the lack of hydrogenation.

The effect of temperature on HDS conversion for Ky #11 mineral matter, 25% Ni, and 50% Ni is shown on Figure 4. The 25% Ni mixture increases linearly by almost 3-fold from 600 to 700 K. The 50 w/o mixture increases 7-fold from 500 to 700 K. It is also obvious that the activity has increased significantly for the Ni-mixtures over the untreated mineral matter. One measure of this is the temperature required for the more active materials to give the same conversion as the mineral matter; i.e. 1% at 683 K. This requires considerable extrapolation, but it is estimated that the 25% Ni mixture would require a temperature of 523 K and the 50 w/o about 453 K.

Another comparison is shown in Figure 5 where log conversion is plotted against the reciprocal temperature. A previously reported curve is shown for presulfided Ky #11 LTA (Morooka and Hamrin, 10) which gave an activation energy of 58.6 kJ/mole. In this study a value of 57.5 kJ/mole was found for H_2-treated Ky #11 which is in good agreement with the earlier value indicating that pretreatment by H_2 or H_2S does not affect the activation energy. Shown on the figure are the data for the 25% Ni mixture which gave a value of 30.4 kJ/mole with a correlation coefficient (r = 0.97). For the 50%

Ni-LTA, a value of 30.3 kJ/mole (r = 0.97) was found. The Ni treatment cut the activation energy almost in half, but increasing the amount of Ni from 25 to 50 w/o had no effect on it.

Additional H_2-treatment on the Ni-modified LTA catalyst increases its HDS activity but decreased its HDN activity. Typical results are given in Table II for the 25% Ni mixture where the HDN activity decreased from 54.7 to 47.5 when additional H_2 treatment of 95 hours was carried out. This may be explained by the increase of cracking activity of the catalyst as the reduction of Ni sites proceeded.

The fact that Ni-added catalyst increased the HDS activity up to 56 times seems due to the high hydrogenation activity of Ni metal which plays an important role on the hydrocracking of thiophene as the first step to give 1,3-butadiene followed by hydrogenation to give n-butenes and butane. On the other hand, since the Ni added catalyst only keeps the HDN activity unchanged implies that the hydrogenation activity of Ni metal does not contribute to the n-butylamine conversion; therefore the n-butylamine HDN conversion is not a hydrocracking reaction but a cracking reaction in which dehydrogenation occurs.

Pyrrole and pyrrolidine pulsing on Ni modified Ky #11 LTA catalyst showed some poisoning effect on the n-butylamine HDN activity while thiophene pulsing increased the HDN activity from 41% to 51% but decreased the selectivity to n-butane.

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TABLE I

Effect of Fe and Ni Modification of Ky #11 LTA
on HDN and HDS Conversions

Addition Compound	w/o Added Element	Surface Area m^2/g	Conversion* HDN	HDS
None	0	32.0	52.0	0.78
$Fe(NO_3)_3 \cdot 9H_2O$	10		38.6	1.98
$FeCl_3 \cdot 6H_2O$	10		48.0	0.96
$NiCl_2 \cdot 6H_2O$	10		48.8	4.73
$Ni(NO_3)_2 \cdot 6H_2O$	10	27.0	53.6	14.0**
$Ni(NO_3)_2 \cdot 6H_2O$	25	31.3	54.7	16.0
$Ni(NO_3)_2 \cdot 6H_2O$	50	28.3	60.7	38.8

* At 673 K, W/F = 2.91 g cat-hr/mole, 4 hr hydrogen pretreatment at 673 K.

** Extrapolated to 0 additional H_2 treatment.

TABLE II

Effect of Additional H_2 Treatment on
HDN Activity of 25% Ni-Ky #11 Mixture

	Additional H_2 Treatment at 673 K, hr			
	0	14	39	95
HDN Conversion From C_4's Produced, %	54.7 ± 0.9	51.0 ± 0.7	50.1 ± 1.3	47.5 ± 1.7
$C_1 - C_3$ By Cracking, %	6.0 ± 0.7	7.4 ± 4.1	11.0 ± 1.1	18.2 ± 1.9
Total Conversion, %	60.7	58.4	61.1	65.7
n-Butane in Total, %	7.9 ± 1.4	9.1 ± 1.1	16.5 ± 3.3	49.6 ± 12.0
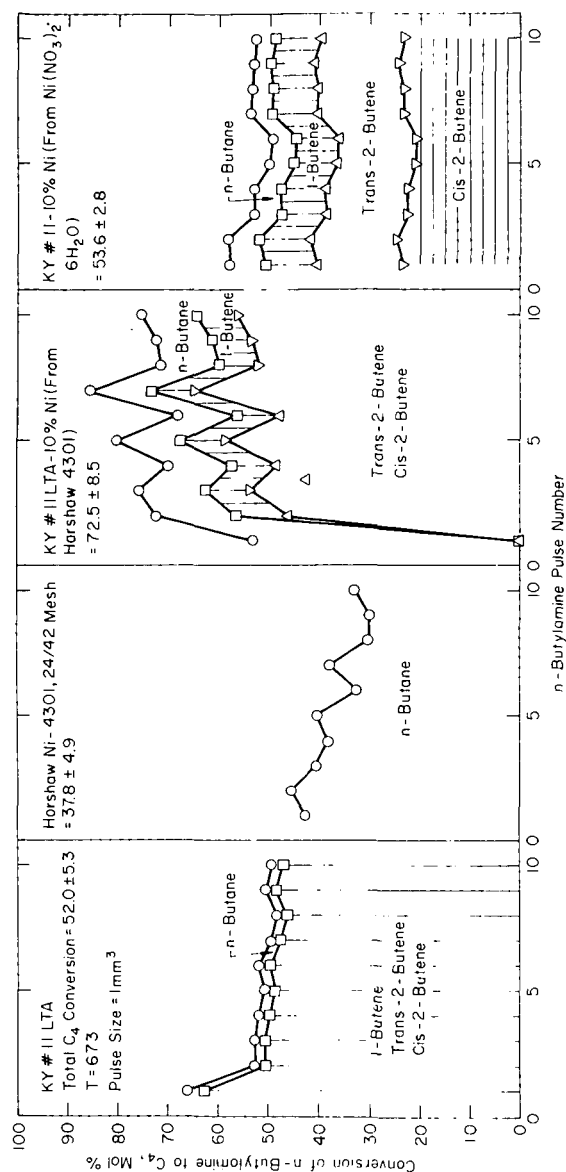
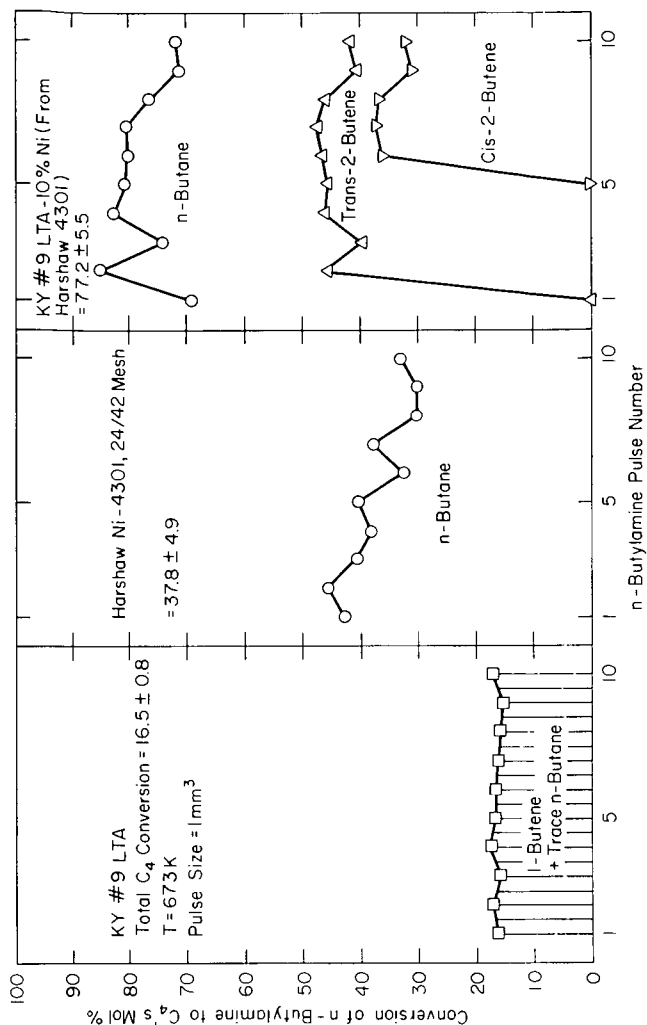Figure 1. HDN Conversion and Selectivity for KY # 11 and Different Nickel Catalysts.

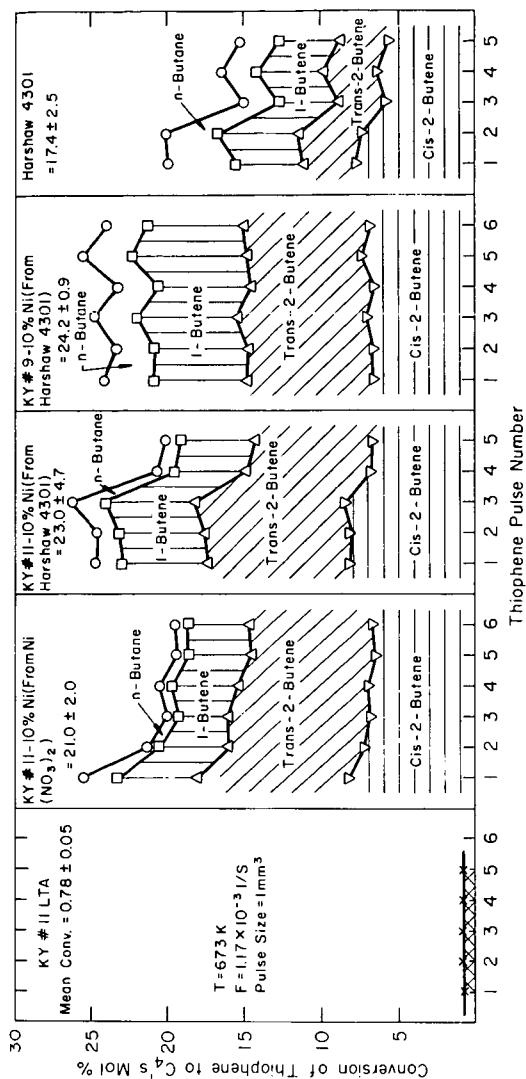Figure 2. HDN Conversion and Selectivity for KY # 9 and Ni Catalysts.

197

Figure 3. HDS Activity and Selectivity for KY LTA-Ni Mixtures with KY # 11 and Harshaw 4301.
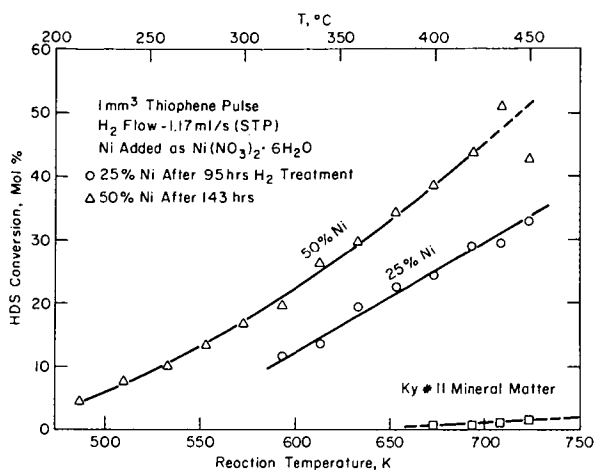
198

Figure 4. HDS Conversion versus Reaction Temperatures
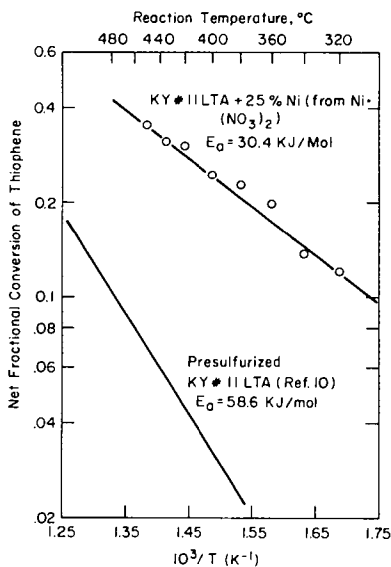for KY # 11 with and without Nickel.

Figure 5. Comparison of Thiophene Conversion - Temperature
Relationships for KY # 11 and KY # 11 - Ni Mixture.

199